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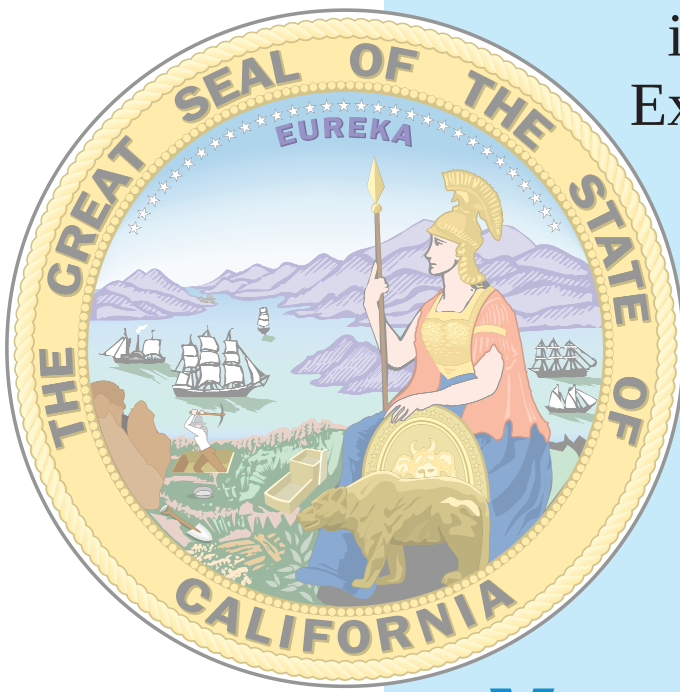
Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate

Report to the California Environmental Policy Council in Response to Executive Order D-5-99



VOLUME 2

Background Information on the Use of Ethanol as a Fuel Oxygenate

State Water Resources Control Board

Air Resources Board

Office of Environmental Health Hazard Assessment

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Volume 2: Background Information on the Use of Ethanol as a Fuel Oxygenate

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Background Information on the Use of Ethanol as a Fuel Oxygenate

1.1. Scope of Report to the California Environmental Policy Council

Governor Gray Davis issued Executive Order D-5-99 on March 25, 1999, calling for the removal of methyl tertiary butyl ether (MTBE) from gasoline at the earliest possible date but no later than December 31, 2002 (State of California, 1999). Task 10 of the Executive Order states "the California Air Resources Board (CARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water, and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA) shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline, and any resulting secondary transformation products. These reports are to be peer reviewed and presented to the Environmental Policy Council by December 31, 1999 for its consideration."

This report has been prepared by the CARB and SWRCB in response to the Executive Order D-5-99 and is divided into five volumes:

- Volume 1: Executive Summary.
- Volume 2: Background Information on the Use of Ethanol as a Fuel Oxygenate.
- Volume 3: Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline.
- Volume 4: Potential Ground and Surface Water Impacts.
- Volume 5: Potential Health Risks of Ethanol in Gasoline.

This Volume 2 provides background information on the use of oxygenated fuels in general, the production of ethanol and its role as a fuel oxygenate, and the physical and chemical properties of ethanol as well as background information on key air and water issues associated with the multimedia evaluation of ethanol as a fuel oxygenate.

1.2. Clean Air Act and the Use of Oxygenated Fuels in California

Under the Clean Air Act (CAA) Amendments of 1990, areas of the country with poor air quality must add an oxygen-containing, organic compound to their gasoline to reduce air emissions. All gasoline sold in the specified, carbon monoxide nonattainment areas during winter months must contain at least 2.7% oxygen (by weight) unless a state obtains a waiver from the U.S. Environmental Protection Agency (US EPA) to implement a different oxygen standard in oxygenated fuel. California's oxygenated gasoline program limits oxygen content to a maximum of 2.2% to limit increases in nitrogen oxides (NOx) emissions that occur from adding oxygen to gasoline (Gomez *et al.,* 1998). Areas that exceed the ozone standard must meet federal requirements for the use of reformulated gasoline (RFG). The CAA requirements for RFG mandate that it must contain a minimum average of 2% oxygen (by weight), no more than 1% benzene (by weight), and no heavy metals. Throughout this report the use of the general term "gasohol" refers to either oxygenated fuel or RFG containing ethanol.

The 1977 CAA Amendments set requirements for "substantially similar gasoline" which mandate oxygenates be approved by the US EPA before they are allowed to be used in gasoline. Ethanol (EtOH), methanol (MeOH), MTBE, and ethyl tertiary butyl ether (ETBE) are currently added to gasoline to meet criteria for the CAA Amendments. Because 10% ethanol by volume blends did not meet the substantially similar definition, the US EPA has granted a waiver for blends of gasoline containing ethanol (Gomez *et al.*, 1998).

MTBE is the most commonly used fuel oxygenate (US EPA, 1999). It is added at 15% by volume to oxygenated fuel or at 11% to RFG and is currently used in over 85% of the nation's reformulated gasoline (US EPA, 1999). Concerns have been raised about the recently discovered widespread distribution of MTBE in ground and surface waters (Moran *et al.*, 1999; Zogorski *et al.*, 1997), consumer complaints of the pungent odor, and possible health effects. (Peaff, 1994; Bedard, 1995).

The state of California has also implemented its own RFG program—the California Cleaner Burning Gasoline (CBG) Program (Gomez, *et al*., 1998). Although MTBE has been the oxygenate used most frequently to meet the goals of this program, up to 10% ethanol (by volume) in gasoline would also be allowed. Currently, about 70% of the gasoline sold in California is RFG (California Energy Commission [CEC], 1999b).

1.3. Requirement for a Multimedia Assessment of New Fuel Components

1.3.1. Regulatory and Legislative Requirements

As required by California Senate Bill 521, the University of California conducted a comprehensive assessment of the current health and environmental impacts of MTBE use in California (Keller *et al.*, 1998). The findings of this assessment formed the basis for Executive Order D-5-99 issued by Governor Davis. That Executive Order precipitated this ethanol fate-and-transport analysis.

United States Environmental Protection Agency Administrator Carol Browner appointed a Blue Ribbon Panel (BRP) in November 1998 to investigate the air-quality benefits and water-quality concerns associated with oxygenates in gasoline and to provide independent advice and recommendations on ways to maintain air quality while protecting water quality (US EPA, 1999). Similar to the requirement in the Executive Order D-5-99, the BRP concluded that the US EPA should conduct a full, multimedia assessment (on air, soil, and water) of any major new additive to gasoline prior to its introduction. The BRP (1999) also recommended the establishment of routine and statistically valid methods for assessing the actual composition of reformulated gasoline and its air quality benefits, including the development of field monitoring and emissions characterization techniques to assess "real world" effects of different blends on emissions.

Recent legislation (Stats. 1999 Ch. 813; SB 529, Bowen) enacted Health and Safety Code Sec. 43840.8, which imposes new requirements regarding multimedia environmental assessments of proposed amendments to ARB's motor vehicle fuels specifications. There is a streamlined environmental review mechanism for amendments proposed prior to January 1, 2000 and adopted prior to July 1, 2000.

California Senate Bill 989 (California State Senate, 1999b) incorporates into state statues most of the provisions of the Governor's MTBE Executive Order. Among the bill's other provisions is the requirement that the SWRCB, on or before June 1, 2000, initiate a specified research program to quantify the probability and environmental significance of releases from petroleum underground storage tank (UST) systems that meet certain upgrade requirements and identify those areas of the state where groundwater is the most vulnerable to MTBE contamination, and to prioritize cleanups based on that identification. Additionally, after January 1, 2000, the bill prohibits the ARB from adopting new fuel specifications until a "multimedia" evaluation has been performed and submitted to the California Environmental Policy Council for final review and approval.

1.3.2. Systems-based Approach to Evaluating New Fuel Components

New fuels or potential additives must be evaluated against not only engine performance and emission requirements but also health and environmental criteria involving airborne toxics and associated health risks, ozone formation potential, and groundwater contamination resulting from production, distribution, and use. A systems-based approach is needed to evaluate risk management trade-offs and to assess health and environmental consequences of the use of ethanol as a fuel oxygenate. A thorough, systems-based approach would include:

1. Identification of the key attributes of gasohol production, distribution, and use, including a fuel-cycle characterization.
2. Screening-level analysis and models to predict the likely environmental fate(s) of ethanol, gasohol, and alkylated-fuel components released into reference landscapes and consideration of potential exposure pathways. This assessment would contain:
   - A review of the existing state of knowledge,
   - The identification of physiochemical properties of the compounds of concern, and
   - Environmental-fate simulations for airborne emissions and subsurface releases.
3. Exposure assessments, including toxicity evaluations of ethanol, gasohol, and alkylated-fuel components that may be released.
4. Identification of key data and knowledge gaps and the specification of the kinds of studies needed to obtain the necessary data and to address any methodological issues related to assessing the use of ethanol, gasohol, and alkylated fuel.
5. Performance of selected experiments to address the identified data gaps.
6. Refinement of conceptual models and integration of new data into critical analyses of environmental transport and fate and multipathway exposures.

1.4. Use of Ethanol as a Transportation Fuel Oxygenate

Ethanol is also widely used in oxygenated gasoline (8% in oxyfuel or 6% in RFG, by volume) because it is a renewable, biomass-based source of fuel and because it is perceived that its environmental impacts are less than those associated with the use of MTBE. To promote markets for ethanol, the United States Congress has approved a 5.4-cents/gal federal subsidy for its use in gasoline. Because of the subsidy, ethanol is sometimes used at 10% by volume in gasoline, even in areas that are not required to use RFG (RFA, 1999).

The use of fuel alcohols as gasoline additives is increasing worldwide, both as a substitute fuel for imported oil, and as oxygenates to minimize air pollution from combustion. In Brazil, for example, approximately one-half of all automobiles run on gasoline containing 22% ethanol with the remainder operating on hydrated ethanol (Petrobrás, 1995). In the United States, gasohol is already available in many states. A recent effort by some members of the House of Representatives to repeal the 5.4-cents/gallon tax subsidy for gasoline with ethanol earlier than its original (year 2000) end date was defeated. Instead, the tax subsidy was extended (*Chemical Market Reporter*, 1998). In addition, ongoing advances in biotechnology will continue to lower ethanol production costs (Lugar and Woolsey, 1999; Carver, 1996).

At the federal level, the BRP was convened in late 1998 to study the benefits and risks of the federal RFG program. In the final BRP report (US EPA, 1999), the Panel recommended that the use of MTBE in the nation's gasoline be substantially reduced. Based on these recommendations, the United States Senate passed a resolution expressing support for a nationwide phase-out of MTBE and supported ethanol as its replacement.

In separate federal initiatives, the use of ethanol as a fuel source is being advocated as a means of promoting the use of renewable biomass fuels. President Clinton signed an Executive Order this year to accelerate the development and use of biomass fuels, products, and chemicals. Joined by the heads of the United States Departments of Agriculture and Energy, US EPA, and Senator Richard Lugar, Clinton announced the goal of tripling the use of bioenergy and bioproducts by 2010 (RFA, 1999).

Illinois Governor George Ryan recently dedicated the first fleet of urban transit buses in the country powered by E-15 Oxygenated Diesel, a blend of ethanol and diesel fuel that shows promise for cleaning up the environment while benefiting rural America. Known as E-15 OxyDiesel, the new fuel is a mixture of 15% ethanol, 80% diesel fuel, and 5% additives. The Illinois governor stated that the E-15 OxyDiesel promises a substantial reduction in black diesel exhaust and its effects, expanded opportunities in the ethanol industry, and new markets for Illinois corn (RFA, 1999). Prior to being tested in Chicago Transit Authority buses, E-15 OxyDiesel was tested in trucks operated by Archer Daniels Midland Corporation.

1.5. Production of Ethanol

The ethanol used for fuel is made primarily from grains or other renewable agricultural and forestry feedstocks (Canadian Renewable Fuels Association [CRFA], 1999). However, any feedstock that contains sugar, starch, or cellulose can be fermented and distilled into ethanol. The fact that ethanol can be made from liquid or solid waste (such as wood byproducts) or agricultural wastes (such as rice straw) is an advantage. In the United States, most ethanol is produced directly from corn (RFA, 1999).

There are basically seven steps in the whole-grain fermentation processes for producing ethanol (American Coalition for Ethanols [ACE], 1999):

1. The grain (such as corn) is milled into a fine powder called meal.
2. The meal is liquefied with the addition of water, enzymes, and heat (120º–150ºC).
3. During the process called saccharification, the liquefied starch is converted to fermentable sugars (dextrose).
4. Yeast is added to ferment the sugars to ethanol and carbon dioxide.
5. The alcohol is distilled to increase the ethanol content from 10% alcohol by volume to about 96%.
6. The alcohol is dehydrated to remove the remaining water. Most distillers use a molecular sieve for this step to produce anhydrous ethanol.
7. The ethanol is then denatured with 2–5% of some product that is added to make it unfit for human consumption. (California is specifying that unleaded gasoline be the denaturant used in fuel-grade ethanol.)

Although some smaller distillers produce ethanol as described above, most larger facilities separate the starch from the grain prior to fermentation ("wet-millers") (ACE, 1999). The use of highly purified starch as the feedstock results in a much cleaner fuel product, whereas the ethanol fuel from whole-grain process contain a lot more impurities (Karaosmanoglu *et al.*, 1996) which do not need to be removed for ethanol to be suitable as a fuel additive.

1.6. Chemical and Physical Properties of Ethanol in Gasoline

Malcolm Pirnie, Inc. (1998) has published a good summary of the physical properties of ethanol compared to MTBE. Ethanol is a small chain molecule (C_2H_5OH) that contains 34.7% oxygen by weight and is infinitely soluble in water. In its pure form, ethanol is a flammable, colorless liquid with a sweet alcohol odor. Ethanol is lighter than water; and if released rapidly in bulk onto water, it will tend to remain on the surface of the water. When gasoline-containing ethanol is in contact with even small quantities of water, the ethanol will separate from the gasoline into the water. Pure ethanol and ethanol blends of gasoline are heavier than unblended gasoline.

Ethanol is very volatile and evaporates into air approximately five times faster than MTBE. Like gasoline vapors, ethanol vapors are denser than air and tend to settle near the ground in low areas. In open-air areas, these vapors disperse rapidly.

When burned, ethanol releases less heat than gasoline. One and a half gallons of ethanol have approximately the same fuel combustion energy as 1 gallon of gasoline. Ethanol has a higher ignition temperature than gasoline (approximately 850°F versus approximately 495°F). When pure ethanol is burned, the flame is less bright than a gasoline flame but is easily visible in daylight. Both ethanol and MTBE have similar octane ratings of about 110 and, when added to gasoline, increase the octane rating. (The long chain, branched hydrocarbon known as octane is used as a standard and is equal to a rating of 100 [Center for Transportation Research, no date]).

Though pure ethanol is poisonous, it is less acutely toxic than the benzene, toluene, ethyl benzene, and xylene (BTEX) components in gasoline. Ethanol is present in pharmaceuticals, mouthwash products, alcoholic beverages, cleaning products, solvents, dyes, and explosives (Verschueren, 1983). Humans frequently ingest fermented beverages that contain about 12% by volume ethanol. Because ethanol is a metabolic byproduct, many organisms tolerate concentrations that may be encountered during accidental releases into the environment (Dagley, 1984). A variety of indigenous microorganisms within the environment are capable of using ethanol as an energy source and will preferentially utilize ethanol over other gasoline hydrocarbons, such as benzene (Alvarez and Hunt, 1999).

Ethanol and ethanol blends of gasoline conduct electricity. In contrast, unblended gasoline is an electrical insulator. For this reason, pure ethanol is more corrosive than gasoline and materials-compatibility must be considered when designing large-volume, bulk-ethanol storage tanks. Aluminum, zinc, tin, lead-based solder, or brass fittings should not be used with pure ethanol or gasoline with high percentages of ethanol. When in contact with liquids that contain high percentages of ethanol, some nonmetallic materials also degrade, including natural rubber, polyurethane, cork-gasket materials, leather, polyester-bonded fiberglass laminate, polyvinyl chloride, polyamides, and methyl-methacrylate plastics (Center for Transportation Research, no date).

1.7. Increased Use of Alkylates as a Transportation Fuel Component

Because the California Energy Commission (CEC, 1999a) anticipates that alkylates[1] will be used in non-oxygenated gasoline and some ethanol-containing gasolines in California to replace the octane[2] normally provided by MTBE, these compounds are also a focus of the analysis included in this report.

Alkylates consist of branched alkanes and cycloalkanes, mostly with 6 to 9 carbons, such as iso-octane (2,2,4-trimethylpentane) and methylcyclopentane. Alkylates are already components in gasoline, but additional amounts will be required to maintain octane levels in gasoline after removal of MTBE, which is a high-octane, anti-knock additive. Even though ethanol also has a high-octane level, its oxygen content is about twice that of MTBE and, consequently, less is required to meet a specified oxygen content (for example, 2.5 wt% oxygen). The resulting octane deficit must be compensated for by adding high-octane blending components, such as alkylates.

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[1] Alkylates are a gasoline blendstock produced by reacting isobutane with light olefins in the presence of strong acid catalysts. They typically consist of branched alkanes, have very low aromatic content, and no sulfur or olefins (Northeast States for Coordinated Air Use Management [NESCAUM], 1999).

[2] MTBE has a 110 octane rating, ethanol has a 115 octane rating; alkylates provide 91 to 99 octane ratings, and aromatic compounds have a 100 octane rating (CEC, 1999a).

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